<Division of Multidisciplinary Chemistry> Molecular Aggregation Analysis

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- Molecular Aggregation Analysis -

http://www.kuicr.kyoto-u.ac.jp/labos/is2/scope.html

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DAOUD, Jamal McGill University, Canada, September–November 2009

Scope of Research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectrosocpies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous sturcutres in mocrocapsules, boipolymers, biological membranes and biological cells.

Research Activities (Year 2009)

Publications

Tsutsumi J, Sasamori T, Yoshida H, Tokitoh N, Sato N, Kato S, Muzikante I, Neilands O: A Noncentrosymmetric Crystal Structure of a Zwitterionic Compound, Pyridinium 5,7-Dihydro-5,7-dioxo-6*H*-cyclopenta[*b*]pyridin-6-ylide, Realized by Weak Hydrogen Bonds, *J. Mol. Struct.*, **920**, 52-60 (2009).

Asami K: Simulation of Dielectric Spectra of Erythrocytes with Various Shapes, *J. Phys. D: Appl. Phys.*, **42**, 135503 (2009).

Presentations

Murdey R, Sato N, The Growth Morphology of Ultrathin Films of Perylene-3,4,9,10-tetracarboxylic Dianhydride (PTCDA) on Rutile (110) Titanium Dioxide, Annual Meeting of Japan Society for Molecular Science 2009 (Nagoya, Japan), 23 September.

Sato N, Uchino Y, Yoshida H, Murdey R, Electronic Structure of Frontier States in an Evaporated Thin Film of Bis(catecholate)diboron, The 5th Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications (Krusenberg, Sweden), 30 September.

Yoshida H, Sato N, Electronic Structure of Buried Interfaces at Organic/Metal Contacts Observed with Angle Resolved X-ray Photoemission Spectroscopy, The 5th Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications (Krusenberg, Sweden), 1 October.

Grants

Yoshida H, The Relation between Electronic Structure and Spin Injection Efficiency at Organic Semiconductor/Metal Interfaces: Towards the Development of Organic Spin Device, Grant-in-Aid for Scientific Research (C), 1 April 2008–31 March 2012.

Asami K, Monitoring of Cell Membrane Disruption and its Repair by Broadband Dielectric Spectroscopy, Grant-in-Aid for Scientific Research (C), 1 April 2009–31 March 2012.

Yoshida H, Preparation of Organic Thin Films with High Crystallinity Using the Supersonic Molecular Beam

A Noncentrosymmetric Crystal Structure of a Zwitterionic Compound, Pyridinium 5,7-Dihydro-5,7-dioxo-6*H*-cyclopenta[*b*]pyridin-6-ylide, Realized by Weak Hydrogen Bonds

An organic polar molecule with definitely deflected charge distribution within a single molecule is called a zwitterionic molecule and attracts much attention because of the potential applicability in optoelectronic devices. Pyridinium 1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylide (PI) is a zwitterionic compound where the pyridine and indandione moieties are positively and negatively charged, respectively. Crystal structures of PI and its derivative compounds where a carbon atom at the 4th or 5th position of the indandione moiety of PI is substituted by a nitrogen atom, that is, 4N-PI or 5N-PI, respectively, were solved with X-ray diffraction analyses. Whereas PI and 5N-PI showed centrosymmetric crystal structures, 4N-PI demonstrated a noncentrosymmetric crystal structure where all the molecules orient to almost the same direction giving a polar crystal as shown in Figure 1. To elucidate the stability of such a polarized structure, we examined interatomic close contacts among the nearest neighbor molecules in the crystals and calculated intermolecular interaction energies with relation to those contacts. As a result, the noncentrosymmetric crystal structure of 4N-PI turns out to be realized by a weak hydrogen bond in the C–H···N manner formed only in the case of this compound (Figure 2).

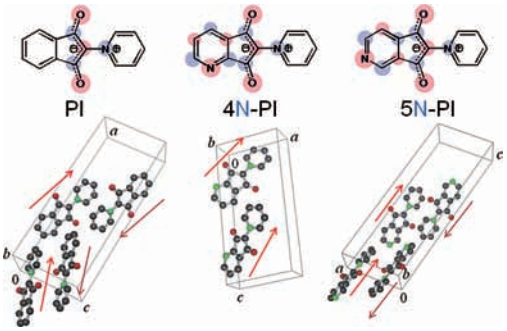

Figure 1. Molecular structures of PI, 4N-PI and 5N-PI and the respective molecular packing manners in the crystals. Blue and red circles indicate positively and negatively charged atoms, respectively. An arrow shows the direction of molecular dipole moment.

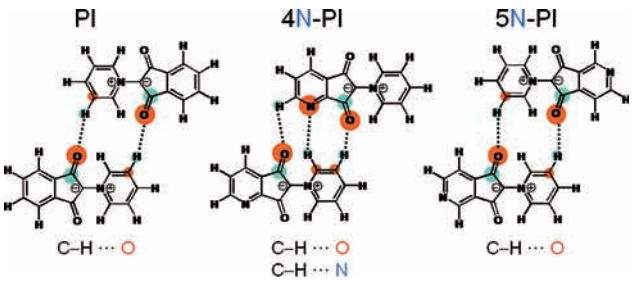

Figure 2. Molecular side-by-side interaction schemes of weak hydrogen bonds (shown by dotted lines) in PI, 4N-PI and 5N-PI crystals.

Effectiveness of 'Thin-Layer' and 'Effective Medium' Approximations in Numerical Simulation of Dielectric Spectra of Biological Cells

The dielectric spectrum of a biological cell suspension is calculated from electric potential distributions in a cell model, which are obtained by solving the Laplace equation. Since analytical solutions of the Laplace equation are limited to simple cell models such as spherical and ellipsoidal shell models, numerical simulation is needed for precise analysis of the dielectric spectrum. However, there are a few concerns when applying numerical techniques. Cells possess membranes of a thickness considerably smaller than the cell size, as well as a cytoplasm including membrane-bound intracellular organelles. The specific and complex cell morphology requires extra fine meshes, which results in considerable computational tasks, especially for 3D simulation. To solve the problems, the 'thin-layer' approximation (TLA) and the 'effective medium' approximation (EMA) were adopted. TLA deals with the membrane as an interface with zero thickness and the specific impedance of the membrane; it was applicable to cells and intracellular organelles of more than 0.1 μm in radius. EMA regards the composite cytoplasm (see Figure 3) as an effective homogeneous phase whose dielectric properties can be calculated separately. Numerical simulation of the dielectric spectra by the finite element method showed that TLA and EMA were both useful in greatly reducing computational tasks without loosing accuracy.

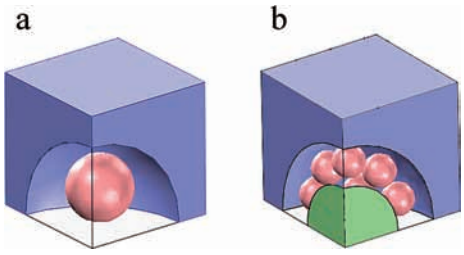

Figure 3. Composite cell models with (a) eight vesicles (red) and with (b) 48 small vesicles (red) surrounding one central large vesicle (green) in the spherical cytoplasm. The blue area is the external medium.

Deposition, The Murata Science Foundation, 1 July 2009–30 June 2010.

Yoshida H, Inverse-Photoemission Spectroscopy with Zero Kinetic Energy Electrons for Measuring the Unoccupied Electronic States of Organic Semiconductors, JST PRESTO, 1 October 2009–31 March 2012.